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### (54) Coated pigment and colorant composition.

(57) A pigment coated with a water-insoluble organic surface modifier can be prepared by:  
(a) preparing a mixture of water and a substantially water-insoluble organic surface modifier;  
(b) introducing the mixture, under pressure, into a conduit having a diameter-decreased portion and a turning portion wherein the diameter-decreased and turning portions provide accelerated flow through the diameter-decreased portion and mutual collision of the accelerated mixture or collision of the accelerated mixture against a wall of the conduit, thereby obtaining an aqueous dispersion in which the surface modifier is homogeneously dispersed in water;  
(c) mixing the aqueous dispersion with a pigment, thereby providing a pigment coated with the surface modifier; and  
(d) isolating the coated pigment.

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## Field of the Invention

5 The present invention relates to a coated pigment formed by coating a pigment with a substantially water-insoluble organic surface modifier and a colorant composition containing the coated pigment. More specifically, it relates to a pigment having suitability for use in a coating composition, an ink, a plastic, a printing dye, a toning agent, a color tone and other coloring materials, and a colorant composition containing the pigment.

## Prior Art of the Invention

10 A pigment is widely used as a colorant composition in the field of coloring materials, and is required to have handling properties and qualities suitable for use in the field. For example, a pigment is required to have dispersibility, fluidity, concentration, gloss, clearness, viscosity, stability with time and other properties suitable for use in the field. For imparting a pigment with these properties, generally, the pigment is surface-coated with an organic surface modifier.

15 Generally, the above surface modification is effectively carried out in an aqueous system, since a pigment is mainly produced in an aqueous system and since the pigment is present in a fine particulate state in an aqueous system without forming dry aggregates. As water-soluble organic surface modifiers, there are known a variety of organic compounds which are to impart a pigment with the above suitable properties. On the other hand, an organic surface modifier which is substantially insoluble in water cannot be used alone in an aqueous 20 system, and some water-insoluble organic surface modifiers have been improved in various ways to apply them to the modification in an aqueous system.

A water-insoluble organic surface modifier in a liquid state is emulsified by a surfactant for use in an aqueous system, or it is emulsified by a rosin for that purpose in JP-A-5-230390. However, only a limited number of water-insoluble organic surface modifiers can be emulsified.

25 When a pigment is surface-modified by an emulsion, the pigment contains a surfactant or a rosin, and may cause bleeding and defective water resistance in a gravure ink or a coating composition, migration in a plastic, or defective emulsification in an ink, and the use of the pigment is limited. Further, an emulsified water-insoluble organic surface modifier may have only an insufficient surface modification effect since it has a large particle diameter as compared with the particle diameter of a pigment.

30 When the water-insoluble organic surface modifier is a solid, a solid pigment is surface-modified by mixing it with the solid modifier since the surface modification cannot be carried out in an aqueous system. However, this surface modification in a solid state is limited to an organic pigment derivative on which the solid modifier itself can be adsorbed. Some substantially water-insoluble solid organic surface modifier having a low melting point may be mixed with a pigment which requires a pigment-forming step of mechanically finely milling it with a kneader, an attritor or a Banbury mixer, such as phthalocyanine blue or dioxazine violet, at a temperature higher than the melting point of the above solid organic surface modifier. The above pigment-forming step is generally carried out around 100°C. since a crystal of the pigment excessively grows at a high temperature. For this reason, the substantially water-insoluble organic surface modifier is used in a semi-solid state for surface-coating a pigment. It is therefore difficult to uniformly coat pigment particles with the modifier, and the surface modification effect thereof is inevitably insufficient. A rosin derivative is the only modifier that is used as a substantially water-insoluble organic surface modifier suitable for use in the above method.

35 The surface modification in the above solid state has a defect in that the modification effect is very low as compared with the modification in an aqueous system in which a modifier is present as fine particles.

## 45 Summary of the Invention

It is an object of the present invention to provide a coated pigment which is highly surface-modified without being restricted by the properties of a water-insoluble organic surface modifier and the affinity of the water-insoluble organic surface modifier to a pigment, and a colorant composition containing the coated pigment.

50 It is another object of the present invention to provide a coated pigment which is highly surface-modified without emulsifying a water-insoluble organic surface modifier with a surfactant or a rosin, and a colorant composition containing the coated pigment.

55 It is further another object of the present invention to provide a coated pigment which is highly surface-modified without treating a pigment and a modifier at a high temperature at which the pigment excessively undergoes the growth of its crystal, and a colorant composition containing the coated pigment.

According to the present invention, there is provided a coated pigment produced by preparing a mixture of water and a substantially water-insoluble organic surface modifier, pressurizing the mixture, introducing the mixture into a flow path having a diameter-decreased portion and a turning portion to cause a shear force in

the mixture of which the flow is accelerated while the mixture is passing the diameter-decreased portion, mutual collision of the mixture of which the flow has been accelerated or collision of the mixture of which the flow has been accelerated against a wall constituting the flow path, thereby obtaining an aqueous dispersion in which the substantially water-insoluble organic surface modifier is homogeneously dispersed in the water, mixing the aqueous dispersion with a pigment to coat the pigment with the substantially water-insoluble organic surface modifier, and isolating the pigment coated with the substantially water-insoluble organic surface modifier.

Further, according to the present invention, there is provided a colorant composition containing the above coated pigment and a vehicle.

10 Brief Description of Drawings.

15 Fig 1 is a schematic cross-sectional view of an ultrahigh-pressure dispersing apparatus in which two portions of a mixture containing water and the substantially water-insoluble organic surface modifier are allowed to collide with each other.

Fig. 2 is a schematic cross-section view of a II-II line portion taken from an ultrahigh-pressure dispersing apparatus shown in Fig. 1.

20 Fig. 3 is a schematic cross-sectional view of an ultrahigh-pressure dispersing apparatus in which two portions of a mixture containing water and the substantially water-insoluble organic surface modifier are allowed to collide with each other.

Fig. 4 is a schematic cross-section view of a IV-IV line portion taken from an ultrahigh-pressure dispersing apparatus shown in Fig. 3.

25 Fig. 5 shows a schematic cross-sectional view of an ultrahigh-pressure in which a mixture containing water and the substantially water-insoluble organic surface modifier is allowed to collide against a wall.

Fig. 6 is a schematic cross-section view of a VI-VI line portion taken from an ultrahigh-pressure dispersing apparatus shown in Fig. 5.

Detailed Description of the Invention

30 The pigment used in the present invention includes an organic pigment and an inorganic pigment. Specifically, the pigment includes those specified as CI pigments in the color index (CI). The pigment used in the present invention preferably has the form of a pigment produced in an aqueous system, for homogeneously and effectively coating it with a substantially water-insoluble organic surface modifier.

35 With regard to a pigment produced in an organic solvent, the organic solvent may be removed and converted to an aqueous dispersion, or a dry powder of the pigment may be dispersed in water with a dispersing apparatus such as a sand mill, a ball mill, an attritor, a paint conditioner or a high-speed mixer, and the aqueous dispersion or the dispersion of the pigment in water may be used in the present invention.

40 The substantially water-insoluble organic surface modifier used in the present invention may be any one of a liquid and a solid at room temperature. For producing the aqueous dispersion, or for producing a high modification effect, it is preferred to use a modifier which is a liquid or which is a solid but is converted to a liquid, preferably a liquid having a low viscosity by heating, as the substantially water-insoluble organic surface modifier.

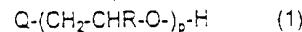
45 The substantially water-insoluble organic surface modifier used in the present invention includes olefinic hydrocarbons, aliphatic carboxylic acids, amine salts or alkyl esters of these, aromatic carboxylic acids, amine salts or alkyl esters of these, synthetic resins, natural resins, rosin derivatives, varnishes, high-molecular-weight dispersing agents, and organic pigment derivatives. These modifiers may be used alone or in combination.

50 Examples of the olefinic hydrocarbons include butadiene, n-paraffin, paraffin wax and olefin wax. Examples of the aliphatic carboxylic acids include higher monocarboxylic acids such as octanoic acid, lauric acid, myristic acid, stearic acid, oleic acid and behenic acid, and dicarboxylic acids such as succinic acid, azelaic acid, sebatic acid, dodecanoic diacid and 1,4-cyclohexanedicarboxylic acid. Examples of the aromatic carboxylic acids include naphthalenedicarboxylic acid, anthraquinonedicarboxylic acid and terephthalic acid. Amine salts or alkyl esters of the above aliphatic carboxylic acids or aromatic carboxylic acids may be also used.

55 Examples of the synthetic resins include polyethylene, polypropylene, polybutadiene, ethylene ionomers, polyvinyl chloride, polyvinylidene chloride, ABS resin, acrylic resin, methacrylic resin, polyvinyl alcohol, cellulose plastics, epoxy resin, polyester resin, phenolic resin, urea resin, melamine resin, polyurethane resin, silicone resin, polyamide resin, polystyrene, polyacetal, polycarbonate, polyphenylene ether, polyphenylene sulfite, polysulfone, polyetherimide, polyether ketone and aniline polymer. Further, natural resins may be used.

Examples of the rosin derivatives include polymerized rosin, rosin amine, rosin ester, oxidized rosin, lime rosin, rosin alkylene oxide adduct, rosin alkyd adduct, and rosin-modified phenol.

The rosin alkylene oxide adduct includes compounds of the following formula (1),

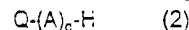


5 wherein Q is a rosin residue, R is hydrogen or an alkyl group having 1 to 3 carbon atoms, and p is an integer of 1 to 30.

The rosin of the above rosin alkylene oxide adduct includes natural rosins such as wood rosin, gum rosin and tall oil rosin, and modified rosins such as polymerized rosin, disproportionated rosin, hydrogenated rosin, oxidized rosin and maleated rosin.

10 The alkylene oxide of the above rosin alkylene oxide adduct preferably includes ethylene oxide, propylene oxide and a mixture of these. The molar amount of the alkylene oxide forming the adduct, per equivalent of the carboxyl group of the rosin, is preferably 1 to 30 mol. When the molar amount of the alkylene oxide is greater than 30 mol, the adduct has high hydrophilic nature so that it can be directly dissolved in water for use as an organic surface modifier without applying the present invention thereto.

15 The rosin alkyd adduct includes compounds of the following formula (2),



wherein Q is a rosin residue, A is an alkyd resin residue and q is an integer of 1 to 30.

The rosin of the rosin alkyd adduct includes natural rosins such as wood rosin, gum rosin and tall oil rosin, and modified rosins such as polymerized rosin, disproportionated rosin, hydrogenated rosin, oxidized rosin and maleated rosin.

20 The alkyd of the rosin alkyd adduct includes those synthesized from polyhydric alcohols such as glycerin, ethylene glycol, triethylene glycol, propylene glycol and pentaerythritol, polyhydric carboxylic acids such as phthalic anhydride and maleic anhydride, and modifiers such as linseed oil, tung oil and soybean oil. The molar amount of the alkyd per equivalent of the carboxyl group of the rosin is preferably 1 to 30 mol.

25 The rosin-modified phenol is obtained by the condensation of a rosin selected from natural rosins such as wood rosin, gum rosin and tall oil rosin and modified rosins such as polymerized rosin, disproportionated rosin, hydrogenated rosin, oxidized rosin and maleated rosin; an alkylphenol selected from phenol, p-tert-butylphenol, p-octylphenol, p-nonylphenol, cresol and bisphenol A; an aldehyde selected from formaldehyde, p-formaldehyde and acetaldehyde; a polyhydric alcohol selected from glycerin, ethylene glycol, triethylene glycol, propylene glycol and pentaerythritol; and optionally polyhydric carboxylic acid selected from phthalic anhydride, maleic anhydride and trimellitic acid, by a conventional method at 200 to 300°C.

30 Examples of the varnishes include offset ink varnish, gravure ink varnish, paint varnish and varnish for a water-based color.

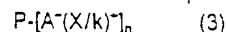
35 The offset ink varnish specifically contains 20 to 50 % by weight of a rosin-modified phenolic resin, a petroleum resin, an alkyd resin or a drying oil-modified resin of any one of these, 0 to 30 % by weight of linseed oil, tung oil or soybean oil, and 10 to 60 % by weight of a solvent such as n-paraffin, isoparaffin, aromatic, naphthalene or an  $\alpha$ -olefin.

40 The gravure ink varnish contains 10 to 50 % by weight of gum rosin, wood rosin, tall oil rosin, lime rosin, rosin ester, a maleic acid resin, a polyamide resin, a vinyl resin, nitrocellulose, cellulose acetate, ethyl cellulose, chlorinated rubber, cyclized rubber, a ethylene-vinyl acetate copolymer, a polyurethane resin, a polyester resin, an alkyd resin, an acrylic resin, gilsonite, dammar, shellac, a mixture of at least two of these resins, a water-soluble resin obtained by water-solubilizing at least one of these resins or a mixture of at least two of these resins or an emulsion resin of at least one of these resins, and 30 to 80 % by weight of a hydrocarbon, an alcohol, a ketone, an ether alcohol, an ether, an ester or water.

45 The paint varnish contains 20 to 80 % by weight of an acrylic resin, an alkyd resin, an epoxy resin, chlorinated rubber, a synthetic resin emulsion, a silicone resin, a fluorine resin, a polyurethane resin, a polyester resin, a melamine resin, a urea resin, a mixture of at least two of these resins, a water-soluble resin obtained by water-solubilizing at least one of these resins or a mixture of at least two of these resins or an emulsion resin of at least one of these resins, and 10 to 60 % by weight of a hydrocarbon, an alcohol, a ketone, an ether alcohol, an ether, an ester or water.

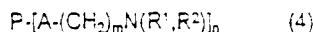
50 Examples of the high-molecular-weight dispersing agents include sulfonic acid amide-containing polymer dispersing agents, hydroxystearic acid-containing polymer dispersing agents and  $\epsilon$ -caprolactam-containing polymer dispersing agents. Specific examples of the high-molecular-weight dispersing agents include a 12-hydroxystearic acid condensate, Solperse 3000, 17000 and 24000 supplied by Zeneca Colours, and BYK-55 160, 161, 162 and 181 supplied by BYK-Chemie GmbH.

55 Examples of the organic pigment derivatives include compounds of the following formulae (3) to (9).

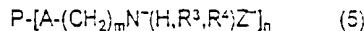


wherein P is an organic dyestuff residue or a heterocyclic resin residue, A is  $-\text{SO}_3$  or  $-\text{COO}$ , X is hydro-

gen, Ca, Ba, Sr, Al, Mn, a primary, secondary or tertiary amine or quaternary ammonium salt containing an alkyl or alkenyl group having 1 to 30 carbon atoms or a primary, secondary, or tertiary amine or quaternary ammonium salt containing an alkyl or alkenyl group having 1 to 30 carbon atoms and containing a polyalkylene oxide having 2 to 5 carbon atoms and having a polymerization degree of 1 to 30, k is a valence of X, and n is an integer of 1 to 4.

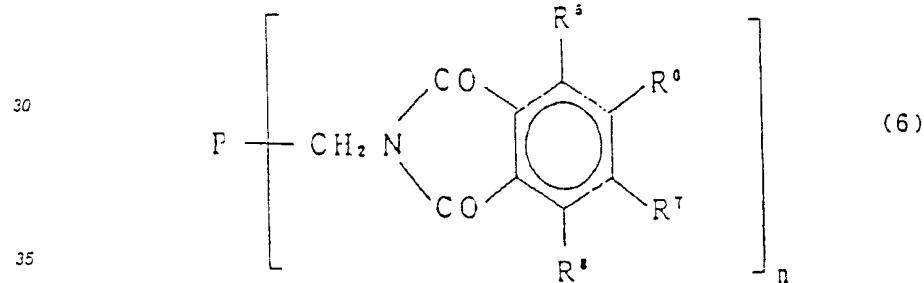


wherein P is an organic dyestuff residue or a heterocyclic ring residue, A is  $-CH_2NH-$ ,  $-SO_2NH-$ ,  $-CH_2NHCOCH_2NH-$ ,  $-CONH-$ ,  $SO_2-$ ,  $-CH_2NHCOCH_2-$ ,  $-CO-$  or a direct bond, each of R<sup>1</sup> and R<sup>2</sup> is independently hydrogen, an alkyl group having 1 to 18 carbon atoms or a substituted alkyl group having 1 to 18 carbon atoms, or a combination of R<sup>1</sup> and R<sup>2</sup> is a heterocyclic ring containing N, O or S, a substituted heterocyclic ring containing N, O or S or an alkylene oxide having 2 to 5 carbon atoms and a polymerization degree of 1 to 30, m is an integer of 0 to 6, and n is an integer of 1 to 4.



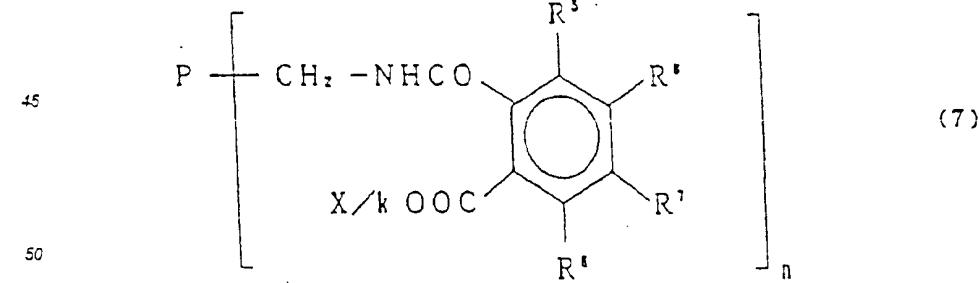
wherein P is an organic dyestuff residue or a heterocyclic ring residue, A is  $-CH_2NH-$ ,  $-SO_2NH-$ ,  $-CH_2NHCOCH_2NH-$ ,  $-CONH-$ ,  $-SO_2-$ ,  $-CH_2NHCOCH_2-$ ,  $-CO-$  or a direct bond, each of R<sup>3</sup> and R<sup>4</sup> is independently hydrogen, an alkyl group having 1 to 18 carbon atoms or a substituted alkyl group having 1 to 18 carbon atoms, or a combination of R<sup>3</sup> and R<sup>4</sup> is a heterocyclic ring containing N, O or S, a substituted heterocyclic ring containing N, O or S or an alkylene oxide having 2 to 5 carbon atoms and a polymerization degree of 1 to 30, Z is alkylbenzenesulfonic acid, alkynaphthalenesulfonic acid, sulfonic acid of higher fatty acid, sulfuric acid ester of olefin, fulfuranic acid ester of higher alcohol, sulfuric acid ester of alkyl phenol, sulfuric acid ester of higher fatty acid, sulfuric acid ester of polyhydric alcohol fatty acid partial ester, phosphate ester of higher alcohol, phosphate ester of alkylphenol, phosphate ester of higher fatty acid, phosphate ester of polyhydric alcohol fatty acid partial ester, polyacrylic acid or polymethacrylic acid, m is an integer of 0 to 6 and n is an integer of 1 to 4.

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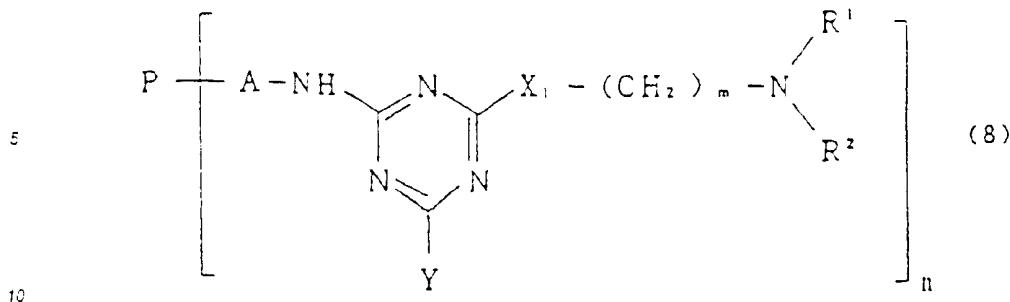


wherein P is an organic dyestuff residue or a heterocyclic ring residue, each of R<sup>5</sup> to R<sup>8</sup> is hydrogen, halogen, nitro, amino, sulfone, carboxyl or lower alkyl, and n is an integer of 1 to 4.

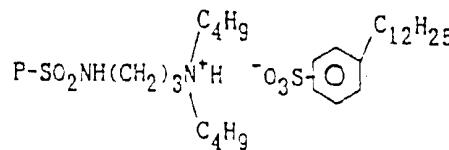
40



wherein P is an organic dyestuff residue or a heterocyclic residue, each of R<sup>5</sup> to R<sup>8</sup> is hydrogen, halogen, nitro, amino, sulfone, carboxyl or lower alkyl, X is hydrogen, a quaternary ammonium salt containing at least one alkyl or alkenyl group having 1 to 20 carbon atoms, Ca, Ba, Sr, Al or Mn, k is a valence of X, and n is an integer of 1 to 4.

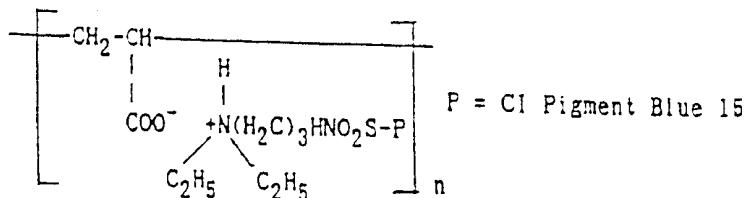


Compound 14



P = CI Pigment Red 48

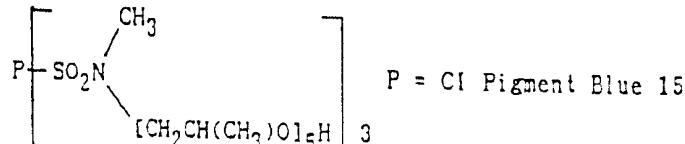
Compound 15



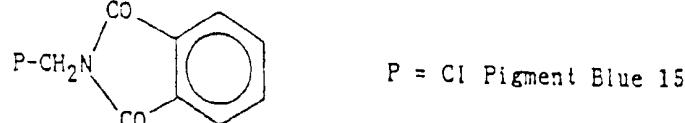
Compound 16 P-SO2NH(CH2CH2O)25H

P = CI Pigment Blue 15

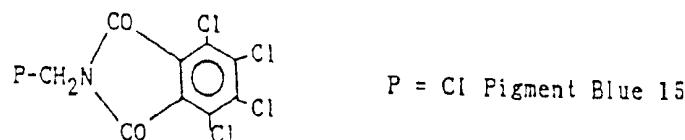
Compound 17



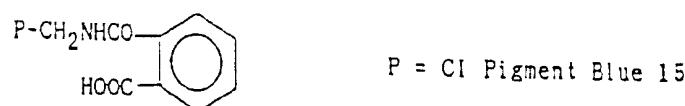
Compound 18



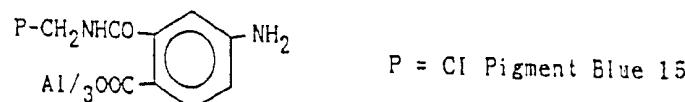
Compound 19



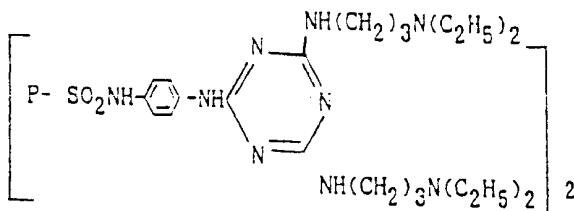
Compound 20



Compound 21



Compound 22



55

Although differing depending upon the field where the pigment is used, generally, the amount of the substantially water-insoluble organic surface modifier per 100 parts by weight of the pigment is preferably 0.5 to 300 parts by weight, more preferably 1 to 200 parts by weight. When this amount is less than 0.5 part by weight, the substantially water-insoluble organic surface modifier shows almost no effect. When it exceeds 300 parts by weight, undesirably, an excess amount of an aqueous dispersion of the substantially water-insoluble organic

surface modifier is sometimes washed away in the steps of filtration and washing the pigment with water or the filter is sometimes clogged with the substantially water-insoluble organic surface modifier.

The aqueous dispersion of the substantially water-insoluble organic surface modifier can be obtained by preparing a preliminary mixture of water and the substantially water-insoluble organic surface modifier and introducing the mixture into an ultrahigh-pressure dispersing apparatus. A surfactant or a rosin emulsion may be added to the mixture so long as the object of the present invention is not impaired.

The ultrahigh-pressure dispersing apparatus is not specially limited so long as the mixture of water and the substantially water-insoluble organic surface modifier can be introduced at least 200 kg/cm<sup>2</sup>. For example, the ultrahigh-pressure dispersing apparatus is selected from a Gaulin homogenizer (supplied by Gaulin Corporation) and a nanomizer (supplied by Nanomizer Inc.).

Figs. 1 to 6 show schematic internal structures of ultrahigh-pressure dispersing apparatus. In Figs. 1 and 2, a mixture containing water and the substantially water-insoluble organic surface modifier is separated and introduced through flow paths 1 and 2 at a pressure of at least 200 kg/cm<sup>2</sup> in an arrow direction, two separated portions of the mixture are allowed to collide with each other near the inlet to a flow path 5, and recovered through the flow path 5. In Fig. 1, numeral 6 is an ultrahigh-pressure dispersing apparatus. The flow path 1 has a diameter-decreased portion 3, and the flow path 2 has a diameter-decreased portion 4. Further, the flow path 5 has a diameter smaller than those of the flow paths 1 and 2. In the diameter-decreased portions 3 and 4, the flow of the mixture is accelerated so that a shear force is exerted on the mixture to promote the dispersing of the mixture. In Figs. 3 and 4, a mixture containing water and the substantially water-insoluble organic surface modifier is separated and introduced through flow paths 7 and 8 at a pressure of at least 200 kg/cm<sup>2</sup> in an arrow direction, and two separated portions of the mixture are allowed to collide with each other near the inlet to a flow path 10, and recovered through the flow path 10. The flow path 7 and the flow path 8 have a diameter-decreased portion 9 toward the inlet to the flow path 10. In Figs. 5 and 6, a mixture containing water and the substantially water-insoluble organic surface modifier is introduced through a flow path 11 at a pressure of at least 200 kg/cm<sup>2</sup>, allowed to collide against a wall 14, passed through a flow path 12, and recovered through a flow path 13. Numeral 15 is a support.

When the substantially water-insoluble organic surface modifier is a liquid at room temperature, the aqueous dispersion is preferably prepared by preparing a mixture of the substantially water-insoluble organic surface modifier and water at room temperature with a high-speed mixer, a homomixer or a low-pressure dispersing apparatus and dispersing the mixture under an ultra-high pressure.

When the substantially water-insoluble organic surface modifier becomes a liquid at a temperature equivalent to, or below, the boiling point of water, the above aqueous dispersion is preferably prepared by heating the substantially water-insoluble organic surface modifier to its melting point, preparing a mixture of the substantially water-insoluble organic surface modifier and water at a temperature equivalent to, or above, the melting point of the substantially water-soluble organic surface modifier, with a high-speed mixer, a homomixer or a low-pressure dispersing apparatus and dispersing the mixture under an ultra-high pressure.

When the substantially water-insoluble organic surface modifier is a solid, it is preferred to prepare a preliminary dispersion of the organic surface modifier in water with a dispersing apparatus such as a sand mill, a ball mill, an attritor, a paint conditioner or a high-speed mixer and introduce the mixture into the flow path for dispersing it under an ultra-high pressure.

Further, part or most of a solid substantially water-insoluble organic surface modifier may be dissolved in an organic solvent before water is added and the mixture is dispersed under an ultra-high pressure.

The amount of the substantially water-insoluble organic surface modifier is properly 1 to 80 % by weight, preferably 5 to 60 % by weight, based on water. The higher the concentration of the organic surface modifier is, the more effective the production is. However, when the above amount exceeds 80 % by weight, it is difficult to obtain an aqueous dispersion. When it is less than 1 % by weight, not only the production efficiency is poor, but also it is difficult to obtain an aqueous dispersion.

The pressure for introducing the mixture of water and the substantially water-insoluble organic surface modifier in the present invention is preferably at least 200 kg/cm<sup>2</sup>. The higher this pressure is, the more stable the resultant aqueous dispersion is. When the above pressure is lower than 200 kg/cm<sup>2</sup>, the substantially water-insoluble organic surface modifier rapidly separates from water so that it is difficult to obtain the aqueous dispersion.

The coated pigment of the present invention can be produced by adding the aqueous dispersion to a pigment and mixing these with stirring. It is preferred to add the aqueous dispersion to an aqueous slurry of the pigment in which particles of the pigment are present in the state of fine particles, since the pigment can be uniformly and effectively coated with the substantially water-insoluble organic surface modifier.

The temperature for the above mixing the aqueous dispersion with the pigment and stirring the mixture is set between room temperature and the boiling point of water as required. After the above mixing and stirring,

it is preferred to carry out the following procedures for some substantially water-insoluble organic surface modifiers. That is, the mixture containing the aqueous dispersion and the pigment is alkalified or acidified or converted to a metal salt or amine salt to precipitate the substantially water-insoluble organic surface modifier on the pigment. However, the substantially water-insoluble organic surface modifier can be fully effectively coated on the pigment by physical adsorption without carrying out the above procedure.

5 The coated pigment is recovered by filtration and washing-with-water steps according to a conventional method. A water-soluble organic surface modifier may be used in combination as required.

10 The coated pigment of the present invention may be used in the state of paste as it is produced, or it may be used in the state of a powder after it is dried or milled.

15 The colorant composition of the present invention is obtained by dispersing the coated pigment of the present invention in a vehicle containing a vehicle resin and/or a solvent. The colorant composition includes an offset ink, a gravure ink, a coating composition, a plastic and a water-based color. The above vehicle is not specially limited, and it may contain an auxiliary and an extender pigment.

20 When the coated pigment of the present invention is dispersed in the vehicle, it is preferred to use a dispersing apparatus such as a dissolver, a high-speed mixer, a homomixer, a sand mill, an attriter, a two-roll mill or a three-roll mill.

25 The coated pigment is generally used in the state of a powder when dispersed in a vehicle. However, when the coated pigment is water-based, or when it is used for an offset ink or polyethylene, the coating pigment in the state of a paste may be directly dispersed in a vehicle without carrying out the step of drying the coated pigment.

30 When the vehicle is for an offset ink, the vehicle contains 20 to 50 % by weight of a rosin-modified phenoic resin, a petroleum resin, an alkyd resin or a drying oil-modified resin of any one of these, 0 to 30 % by weight of linseed oil, tung oil or soybean oil, and 10 to 60 % by weight of a solvent such as n-paraffin, isoparaffin, aromatic, naphthene or an  $\alpha$ -olefin.

35 When the vehicle is for a gravure ink, the vehicle contains 10 to 50 % by weight of gum rosin, wood rosin, tall oil rosin, lime rosin, rosin ester, a maleic acid resin, a polyamide resin, a vinyl resin, nitrocellulose, cellulose acetate, ethyl cellulose, chlorinated rubber, cyclized rubber, a ethylene-vinyl acetate copolymer, a polyurethane resin, a polyester resin, an alkyd resin, an acrylic resin, gilsonite, dammar, shellac, a mixture of at least two of these resins, a water-soluble resin obtained by water-solubilizing at least one of these resins or a mixture of at least two of these resins or an emulsion resin of at least one of these resins, and 30 to 80 % by weight of a hydrocarbon, an alcohol, a ketone, an ether alcohol, an ether, an ester or water.

40 When the vehicle is for a coating composition, the vehicle contains 20 to 80 % by weight of an acrylic resin, an alkyd resin, an epoxy resin, chlorinated rubber, a synthetic resin emulsion, a silicone resin, a fluorine resin, a polyurethane resin, a polyester resin, a melamine resin, a urea resin, a mixture of at least two of these resins, a water-soluble resin obtained by water-solubilizing at least one of these resins or a mixture of at least two of these resins or an emulsion resin of at least one of these resins, and 10 to 60 % by weight of a hydrocarbon, an alcohol, a ketone, an ether alcohol, an ether, an ester or water.

45 The vehicle for plastics includes polyethylene, polypropylene, polybutadiene, ethylene ionomer, polyvinyl chloride, polyvinylidene chloride, ABS resin, acrylic resin, methacrylic resin, polyvinyl alcohol, cellulose-based plastic, epoxy resin, polyester resin, phenolic resin, urea resin, melamine resin, polyurethane resin, silicone resin, polyamide resin, polystyrene, polyacetal, polycarbonate, polyphenylene ether, polyphenylene sulfite, polysulfone, polyetherimide, polyether ketone and complexes of these.

50 The vehicle for a water-based color contains at least one of nonionic, anionic and cationic surfactants or sulfonic acid amide-containing, hydroxystearic acid-containing and  $\epsilon$ -caprolactam-containing high-molecular-weight dispersing agents, a polyhydric alcohol selected from glycerin, ethylene glycol, triethylene glycol, propylene glycol and pentaerythritol, water, and optionally an amine, an antiseptic and an antifoaming agent.

55 According to the present invention, a predetermined amount of the substantially water-insoluble organic surface modifier is mixed with a predetermined amount of water, the resultant mixture is pressurized, and introduced into an ultrahigh-pressure dispersing apparatus having a flow path diameter-decreased portion and a turning portion at a pressure of at least 200 kg/cm<sup>2</sup>, to cause a shear force in the mixture of which the flow is accelerated while the mixture is passing the diameter-decreased portion, mutual collision of the mixture of which the flow has been accelerated and collision of the mixture of which the flow has been accelerated against a wall constituting the flow path, whereby an aqueous dispersion of which the preparation has been impossible can be obtained in the absence of a surfactant or a rosin emulsion or in the presence of a surfactant or a rosin emulsion in such a small amount that the object of the present invention is not impaired. It is considered that the substantially water-insoluble organic surface modifier is finely pulverized to a molecular level by the collision under a high pressure to form a stable aqueous dispersion owing to an intermolecular attracting force between water and the substantially water-insoluble organic surface modifier.

In the present invention, the substantially water-insoluble organic surface modifier which is finely pulverized as described above is mixed with a pigment, whereby the surface of each particle of the pigment is coated with molecules of the substantially water-insoluble organic surface modifier. Therefore, the present invention produces a remarkably effective surface modification effect with the substantially water-insoluble organic surface modifier in a small amount as compared with the conventional coating of a pigment with emulsion particles.

### 5 Examples

The present invention will be detailed hereinafter with reference to Examples, in which "part" and "%" stand for "part by weight" and "% by weight".

#### 10 Example 1

A mixture of 50 parts of water and 50 parts of an adduct of 1 mol of rosin with 3 mol of propylene oxide was heated to 80°C, and introduced into a nanomizer (supplied by Nanomizer Inc.) at a pressure of 1,000 kg/cm<sup>2</sup> to disperse the mixture in the nanomizer. This introduction for the dispersing in the nanomizer was repeated three times to give an aqueous dispersion. 10 Parts of the aqueous dispersion was added to a water-based slurry prepared by dispersing 100 parts, as a dry product, of a CI Pigment Blue 15:3 (obtained by forming copper phthalocyanine into a pigment by a conventional method using a kneader and removing a kneading aid) in 1,000 parts of water, and the mixture was stirred for 30 minutes, filtered, washed with water and dried to give 103 parts of a coated pigment.

The above-obtained coated pigment was excellent in dispersibility. That is, it gave an offset ink having an average particle size (measured with a grindometer) of less than 5 µm by dispersing it with a three-roll mill twice, while a coated pigment obtained in Comparative Example 1 to be described below required the above dispersing treatment three times.

#### 15 Comparative Example 1

A copper phthalocyanine was formed into a pigment in the same manner as in Example 1. In this case, 5 parts of an adduct of 1 mol of rosin with 3 mol of propylene oxide was added when the kneading was completed 90 %, and the mixture was co-kneaded for a remaining kneading time of 10 %. A kneading aid was removed, and the remainder was filtered, washed with water and dried to give 103 parts of a coated pigment.

#### 20 Comparative Example 2

A mixture of 50 parts of water and 50 parts of an adduct of 1 mol of rosin with 3 mol of propylene oxide were heated to 80°C, and introduced into a nanomizer (supplied by Nanomizer Inc.) at a pressure of 100 kg/cm<sup>2</sup> to disperse the mixture in the nanomizer. This introduction for the dispersing in the nanomizer was repeated five times, while no aqueous dispersion was obtained since an oil layer and an aqueous layer separated promptly. The same mixture as above was dispersed with a homomixer, or dispersed with a sand mill, to give no aqueous dispersion. That is, no aqueous dispersion was obtained for treating a pigment in an aqueous system.

#### 25 Example 2

50 Parts of an adduct of 1 mol of rosin with 3 mol of propylene oxide was mixed with a mixture containing 25 parts of water and 25 parts of methyl alcohol with stirring, to prepare a semi-solution. The semi-solution at 25°C was treated by introducing it into a nanomizer (supplied by Nanomizer Inc.) at a pressure of 1,000 kg/cm<sup>2</sup> three times, and thereafter, 103 part of a coated pigment was obtained in the same manner as in Example.

The above-obtained coated pigment was excellent in dispersibility. That is, it gave an offset ink having an average particle size (measured with a grindometer) of less than 5 µm by dispersing it with a three-roll mill twice.

#### 30 Example 3

55 A mixture of 70 parts of water and 30 parts of an alkyd varnish for an offset ink was heated to 80°C, and introduced into a nanomizer (supplied by Nanomizer Inc.) at a pressure of 1,700 kg/cm<sup>2</sup> and treated with the nanomizer. This introduction for the dispersing in the nanomizer was repeated three times to give an aqueous

dispersion. 40 Parts of the aqueous dispersion was added to a water-based slurry prepared by dispersing 100 parts, as a dry product, of a CI Pigment Red 57:1 (synthesized by a conventional method) in 2,000 parts of water, and the mixture was stirred at 70°C for 30 minutes, filtered, washed with water and dried to give 103 parts of a coated pigment in the form of a paste.

5 The above coated pigment showed excellent suitability for emulsification. That is, an emulsion of an offset ink containing the above coated pigment showed a surface tension of 67  $\mu$ S/cm, while the counterpart obtained in Comparative Example 3 to be described later showed a surface tension of 55  $\mu$ S/cm.

#### Comparative Example 3

10

While a solution containing 80 parts of water and 2 parts of sodium hydroxide was boiled, 10 parts of disproportionated rosin was added to the solution to prepare a rosin solution. The rosin solution was cooled to room temperature, 10 parts of the same alkyd varnish as that used in Example 3, and the mixture was stirred with a high-speed mixer to give a solution of alkyd and rosin in the form of a semi-solid-dissolved solution. Then, 15 120 parts, as a dry product, of a coated pigment in the form of a paste was obtained in the same manner as in Example 3 except that the aqueous dispersion was replaced with 120 parts of the above solution of alkyd and rosin.

15

#### Example 4

20

A mixture of 50 parts of water and 50 parts of a hydroxystearic acid-containing polymer dispersing agent (Solsperser 17000, supplied by Zeneca Colours) was heated to 80°C, and introduced to a Gaulin homogenizer (supplied by Gaulin) at a pressure of 500 kg/cm<sup>2</sup> and treated with the Gaulin homogenizer to give an aqueous dispersion. 10 Parts of the aqueous dispersion was added to a water-based slurry prepared by dispersing 100 parts of powdery CI Pigment Violet 19 in 2,000 parts of water with a beads mill, and the mixture was stirred at 70°C for 30 minutes. The mixture was adjusted to a pH of 10, filtered, washed with water and dried to give 103 parts of a coated pigment.

An oil coating composition containing the above coated pigment was prepared (the preparation method will be described later) and measured for a viscosity to show 800 cps. The counterpart obtained in Comparative Example 4 to be described later showed a viscosity of 2,000 cps. The oil coating composition thus had an excellent viscosity. For reference, the same pigment as the above was measured for a viscosity to show 3,000 cps. In addition, the viscosity was measured with a Brookfield viscometer at 6 rpm.

25

#### Comparative Example 4

30

An oil coating composition was obtained in the same manner as in Example 4 except that the 10 parts of the aqueous dispersion was replaced with 5 parts of Solsperser.

35

#### Comparative Example 5

40

An attempt was made to dissolve the same hydroxystearic acid-containing high-molecular-weight dispersing agent as that used in Example 4 in water in the presence of an acid, an alkali or a surfactant, while no solution was obtained. Further, an attempt was made to disperse the same hydroxystearic acid-containing high-molecular-weight dispersing agent in water with a high-speed mixer or a sand mill, while no aqueous dispersion was obtained. That is, no aqueous dispersion was obtained for treating a pigment in an aqueous system.

45

#### Example 5

50

A preliminary dispersion prepared by dispersing 10 parts of a copper phthalocyanine derivative of P- $\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2$  (wherein P was CI Pigment Blue 15) in 90 parts of water with an attritor was introduced into a nanomizer supplied by Nanomizer Inc. at a pressure of 1,300 kg/cm<sup>2</sup> and treated with the nanomizer. This introduction and treatment was repeated three times to give an aqueous dispersion. 50 Parts of the aqueous dispersion was added to a water-based slurry prepared by dispersing 100 parts, as a dry product, of CI Pigment Blue 15:1 (prepared by forming a copper phthalocyanine into a pigment by a conventional method using sulfuric acid and then removing the sulfuric acid) in 1,000 parts of water, and the mixture was stirred at 80°C for 30 minutes, filtered, washed with water and dried to give 103 parts of a coated pigment.

55

An oil coating composition containing the above coated pigment showed an excellent viscosity. That is, the oil coating composition showed a viscosity of 150 cps, while the counterpart obtained in Comparative Ex-

ample 6 to be described later showed a viscosity of 600 cps, and the counterpart obtained in Comparative Example 7 to be described later showed a viscosity of 420 cps. Further, the pigment (CI Pigment Blue 15:1) not treated with the pigment derivative showed a viscosity of 2,700 cps.

5 Comparative Example 6

An alkyd melamine coating composition was obtained in the same manner as in Example 5 except that the aqueous dispersion was replaced with 5 parts of the same pigment derivative as that used in Example 5.

10 Comparative Example 7

15 104 Parts of a coated pigment was obtained by mixing a dispersion of 10 parts of a copper phthalocyanine derivative of  $P\text{-SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2$  (wherein P was CI Pigment Blue 15) in 90 parts of water with a slurry of 100 parts of a pigment (CI Pigment Blue 15:1) in 1,000 parts of water with a mixer.

15 Example 6

20 A mixture of 80 parts of water and 20 parts of powdery polypropylene was introduced to a nanomizer (supplied by Nanomizer Inc.) at a pressure of 1,500 kg/cm<sup>2</sup> and treated in the nanomizer. This introduction and treatment was repeated five times to give an aqueous dispersion. 500 Parts of the aqueous dispersion was added to a water-based slurry prepared by dispersing 100 parts, as a dry product, of CI Pigment Blue 15:3 (prepared by forming copper phthalocyanine into a pigment by a conventional method using a kneader, and removing a kneading aid) in 1,000 parts of water, the mixture was stirred for 30 minutes, filtered, washed with water and dried to give 196 parts of a coated pigment.

25 The so-obtained coated pigment and a polypropylene resin were mixed with a tumbler, and the resultant composition was injection-molded to give a molded article of the composition. The molded article had a color strength higher, by 24 %, than that of a molded article prepared in Comparative Example 8 to be described later, or showed excellent color development. The molded article obtained in this Example was measured for an L value with a color machine, and a sample obtained in Comparative Example 8 to be described later was measured for an L value with the color machine. The difference between these two L values,  $\Delta L$ , was calculated to show that the color strength of the coated pigment in this Example was higher, by 24 %, than the pigment prepared in Comparative Example 8, or the coated pigment showed excellent color development (The coated pigment in this Example showed the same color density as that of the pigment in Comparative Example 8 even when the amount of the coated pigment in this Example was smaller by 24 % by weight).

35 Comparative Example 8

40 CI Pigment Blue 15:3 and the same polypropylene resin as that used in Example 6 were mixed with a tumbler in the same mixing ratio as that in Example 6, and the resultant composition was injection-molded to give a molded article.

Examples 7 - 32

45 Aqueous dispersions were prepared in the same manner as in Example 1 except that the pressure for the introduction of mixtures into a nanomizer was changed as shown in Table 1, and pigments shown in Table 1 were treated with the aqueous dispersions to obtain colorant compositions shown in Table 1.

50

55

Table 1

		Aqueous Dispersion		Pigment Composition		Colorant Composition	Effects
	Organic surface modifier	Concentration (%)	Pressure (kg/cm <sup>2</sup> )	CI	Aqueous Pigment dispersion (100 parts)	(part)	
10	Ex.7 Paraffin wax	30	1,000	Red 57:1	20	offset plastic	fluidity dispersibility
	Ex.8 Polyethylene wax	30	1,000	Violet 23	20		
15	Ex.9 Stearic acid	50	800	Blue 15:3	10	coating composition	viscosity
	Ex.10 Oleic acid amide	50	800	Blue 15:3	6	offset	fluidity
20	Ex.11 Sebastic acid	50	800	Blue 15:3	6	offset	fluidity
	Ex.12 Laurylamine	70	1,300	Yellow 12	4	offset	fluidity
	Ex.13 Distearyl-dimethyl quaternary ammonium chloride	60	1,300	Red 57:1	8	gravure	gloss
25	Ex.14 Polystyrene	10	1,000	Blue 15:3	100	plastic	heat resistance
	Ex.15 Styrene/acrylic resin	10	1,000	Blue 15:3	50	water-based	fluidity
30						coating composition	
	Ex.16 Aniline polymer	20	1,000	Blue 15:3	25	coating composition	weatherability
35	Ex.17 Poly-methacrylic acid	10	1,000	Violet 19	50	coating	weatherability
	Ex.18 Polymerized rosin*1	20	400	Blue 15:3	20	offset	roll-baking
40	Ex.19 Rosin ester*2	20	400	Blue 15:3	20	offset	dispersibility
	Ex.20 Rosinamine*3	40	1,000	Yellow 12	12	offset	fluidity
	Ex.21 Rosin-modified phenol*4	10	800	Red 57:1	100	offset	clearness
45	Ex.22 Acryl varnish for gravure	30	1,700	Violet 23	30	gravure	gloss
	Ex.23 Polyester varnish for coating composition	30	1,700	Blue 60	30	coating composition	viscosity
50							

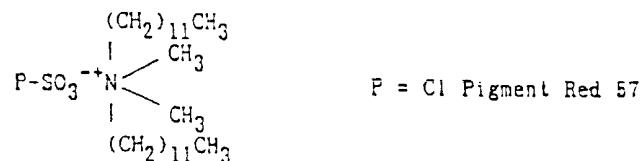
Ex. = Example

5	Aqueous Dispersion		Pigment		Colorant		Effects
	Organic surface modifier	Concen- tration (°C)	Pressure (kg/cm <sup>2</sup> )	CI Composition Pigment dispersion (100 parts)(part)	Aqueous Pigment dispersion (100 parts)(part)	Colorant Composition (part)	
10	Ex.24 High- molecular- weight dispersing agent*5	60	1,000	Red 177	10	coating composition	viscosity
15	Ex.25 12-Hydroxy- stearic acid condensate	40	1,300	Blue 15:1	10	coating composition	viscosity
20	Ex.26 Phthalimide- methyl copper phthalocyanine	10	1,300	Blue 15:3	100	plastic	heat resistance
25	Ex.27 Copper phthalocyanine sulfonic acid	10	1,300	Blue 15:3	50	gravure	gloss
30	Ex.28 Compound (A)*6	10	1,300	Red 57:1	100	offset	fluidity
	Ex.29 Compound (B)*7	10	1,300	Red 48:1	80	gravure	gloss
	Ex.30 Compound (C)*8	10	1,300	Violet 23	100	water-	density
	Ex.31 Compound (D)*9	10	1,300	Blue 15:1	100	based color	
	Ex.32 Compound (E)*10	10	1,300	Yellow 154	100	coating composition	viscosity
						coating composition	viscosity

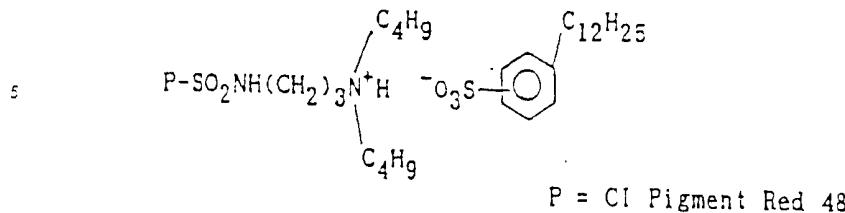
Ex. = Example

35 Notes: \*1: Sylbatac 95 (supplied by Arakawa Chemical Ind. Ltd.)  
\*2: Estergum AT (supplied by Arakawa Chemical Ind. Ltd.)  
\*3: Rosinamine D (supplied by Rika Hercules Inc.)  
\*4: Tamanol 361 (supplied by Arakawa Chemical Ind. Ltd.)  
\*5: BYK-160 (supplied by BYK Chemie GmbH)

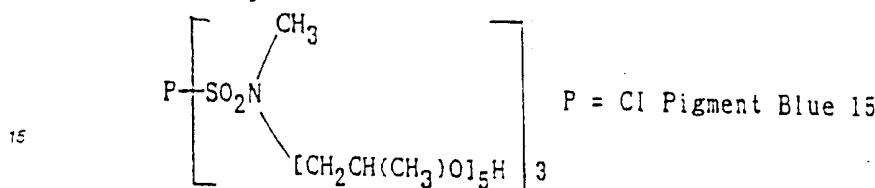
\*6: Compound A



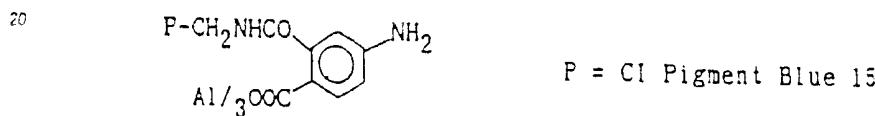
## \*7: Compound B



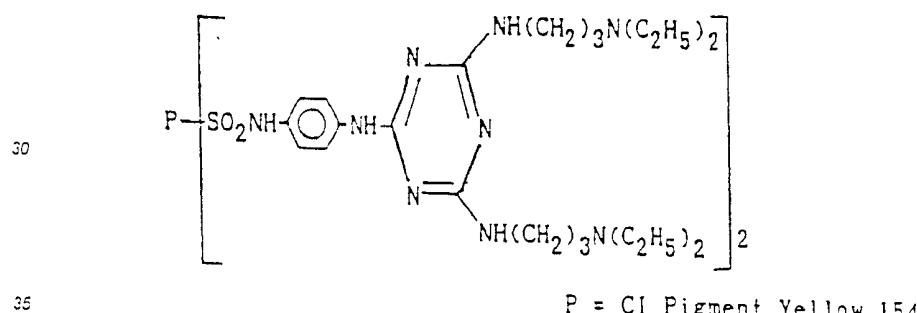
## \*8: Compound C



## \*9: Compound D



## \*10: Compound E



- Amount of aqueous dispersion (part) per 100 parts by weight of pigment
- 40 • Roll baking = a phenomenon in which a pigment strongly adheres to a roll when an offset ink is prepared by dispersing with a roll mill. When a pigment has poor dispersibility, this phenomenon is liable to occur.
- 45 • Coating composition in the column of Colorant Composition refers to an oil coating composition.

## 50 Preparation Example (Offset ink)

16 Parts of a pigment and 54 parts of a modified phenolic resin were mixed, and the mixture was dispersed with a three-roll mill to prepare a base ink. 20 Parts of a rosin-modified phenolic resin and 10 parts of a solvent for an offset ink were mixed with the base ink to give an offset ink.

## 55 Preparation Example (Gravure ink)

10 Parts of a pigment, 70 parts of a nitrocellulose varnish and 20 parts of ethyl acetate were placed in a

225-ml glass bottle together with 300 g of 3 mmΦ steel balls, and dispersed with a paint conditioner for 1 hour to give a gravure ink.

Preparation Example (Oil coating composition)

5

10 Parts of a pigment, 52 parts of an alkyd resin varnish (nonvolatile content 60 %), 23 parts of a melamine resin varnish (nonvolatile varnish 50%) and 15 parts of xylene were placed in a 225-ml glass bottle together with 300 g of 3 mmΦ steel balls, and dispersed with a paint conditioner for 1 hour to give an oil coating composition.

10

Preparation Example (Water-based coating composition)

15

10 Parts of a pigment, 12.5 parts of a solution of an acrylic resin having average molecular weight of 25,000 and an acid value of 60 (nonvolatile content 20 %) and 20 parts of ion-exchanged water were placed in a 225-ml glass bottle together with 150 g of 3 mmΦ steel balls, and dispersed with a paint conditioner for 3 hours. Then, 37.5 parts of the same acrylic resin as that described above and 4.3 parts of a methylated melamine resin were added to the dispersion to give a water-based coating composition.

20

Preparation Example (Plastic colorant composition)

25

0.1 Part of a pigment, 100 parts of a polypropylene resin and 0.1 part of zinc stearate were mixed with a tumbler, and the mixture was injection-molded to give a colorant composition of polypropylene resin.

25

Preparation Example (Water-based color)

30

15 Parts of a pigment, 6 parts of ethylene glycol, 29 parts of water and 10 parts of a nonionic surfactant were placed in a 225-ml glass bottle together with 100 g of 3 mmΦ steel balls, and dispersed with a paint conditioner for 2 hours, and then 40 parts of water was added to give a water-based color.

30

3 Parts of the above water-based color was mixed with 60 parts of an acrylic resin-containing binder for dyeing to give a color for dyeing.

35

As explained above, the present invention can utilize, as a surface modifier, a substantially water-insoluble organic substance in the form of any one of a solid and a liquid which cannot be used in conventional methods, and produces excellent effects on surface modification. The coated pigment of the present invention contains neither a surfactant nor a rosin emulsion, so that it is free from adversary effects caused by the surfactant or rosin emulsion, and can be used as a colorant composition without being limited in use.

## Claims

- 40 1. A process for producing a coated pigment which process comprises:
  - (a) preparing a mixture of water and a substantially water-insoluble organic surface modifier;
  - (b) introducing the mixture, under pressure, into a conduit having a diameter-decreased portion and a turning portion wherein the diameter-decreased and turning portions provide accelerated flow through the diameter-decreased portion and mutual collision of the accelerated mixture or collision of the accelerated mixture against a wall of the conduit, thereby obtaining an aqueous dispersion in which the surface modifier is homogeneously dispersed in water;
  - (c) mixing the aqueous dispersion with a pigment, thereby providing a pigment coated with the surface modifier; and
  - (d) isolating the coated pigment.
- 45 2. A process according to claim 1, wherein the surface modifier is selected from olefinic hydrocarbons, aliphatic carboxylic acids, amine salts or alkyl esters of aliphatic carboxylic acids, aromatic carboxylic acids, amine salts or alkyl esters of aromatic carboxylic acids, synthetic resins, natural resins, rosin derivatives, varnishes, high-molecular-weight dispersing agents, organic pigment derivatives, and mixtures thereof.
- 50 3. A process according to claim 1 or 2, wherein the surface modifier is a liquid or a solid at room temperature.
- 55 4. A process according to any one of the preceding claims, wherein the conduit comprises at least two flow

paths into which portions of the mixture are introduced, a diameter-decreased section of the conduit where the two portions of the mixture collide with each other and a flow path through which the mixture is recovered.

- 5 5. A process according to any one of claims 1 to 3 wherein the conduit has one flow path into which the mixture is introduced and at least one flow path through which the mixture is recovered.
- 10 6. A process according to any one of the preceding claims, wherein the concentration of the surface modifier in the mixture is from 1 to 80 % by weight based on water.
- 15 7. A process according to any one of the preceding claims wherein, in step (b), the mixture collides against a wall of the conduit and two portions of the mixture collide with each other.
8. A process according to any one of the preceding claims, wherein, in step (b), the mixture is introduced into the conduit at a pressure of at least 200 kg/cm<sup>2</sup>.
- 15 9. A coated pigment obtainable by a process according to any one of claims 1 to 8.
- 10 10. A colorant composition containing a coated pigment according to claim 9 and a vehicle.
- 20 11. A composition according to claim 10, wherein the vehicle is a vehicle for an offset ink.
12. A composition according to claim 10, wherein the vehicle is a vehicle for a gravure ink.
- 25 13. A colorant composition according to claim 10, wherein the vehicle is a vehicle for a coating composition.
14. A composition according to claim 10, wherein the vehicle is a vehicle for plastics.
15. A composition according to claim 10, wherein the vehicle is a vehicle for a water-based color.

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FIG. 1

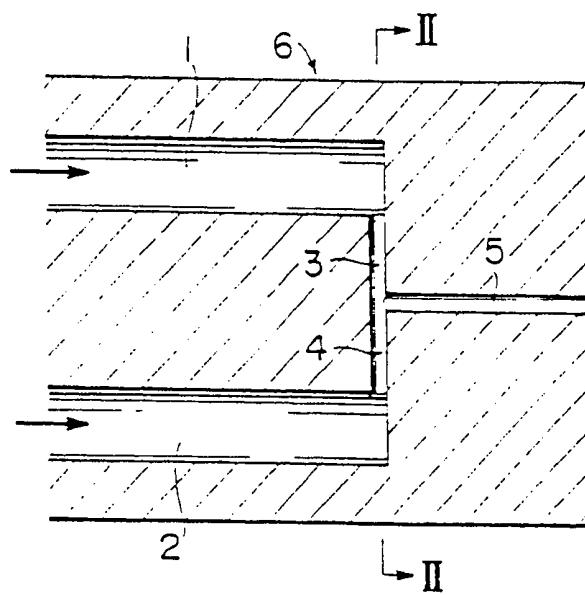


FIG. 2

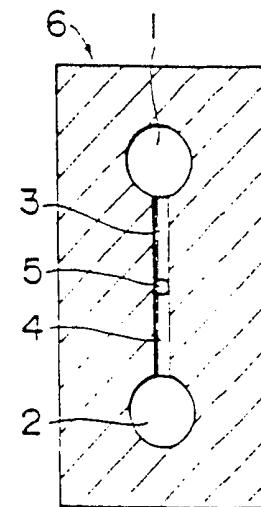


FIG. 3

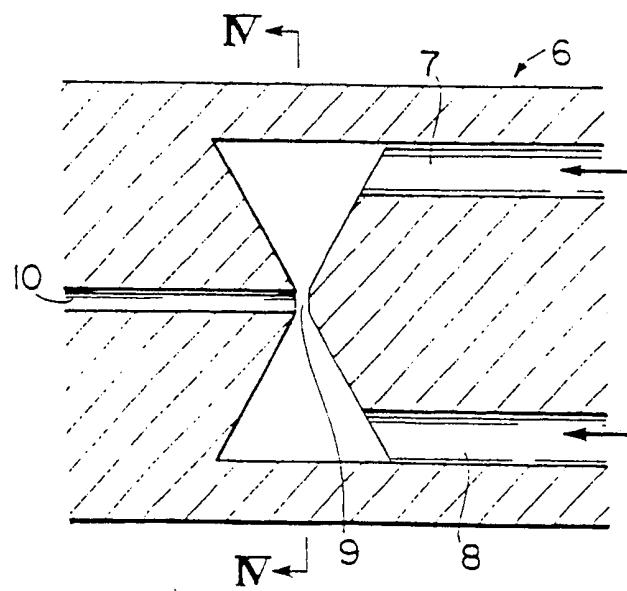


FIG. 4

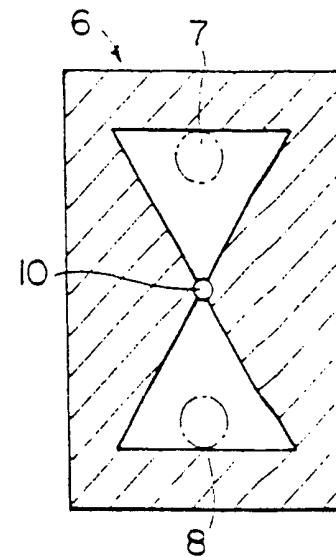


FIG. 5

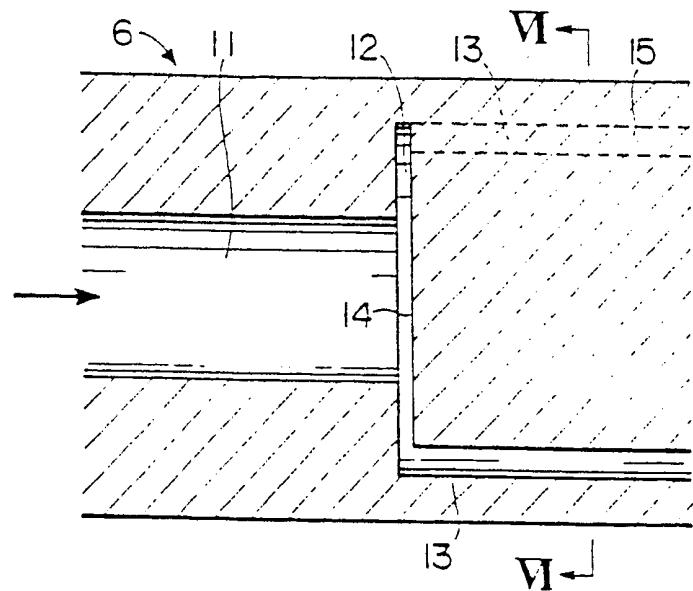
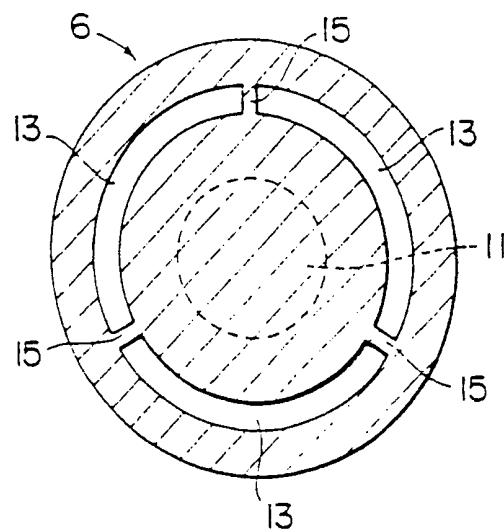


FIG. 6



(19)



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### (§4) Coated pigment and colorant composition

(57) A pigment coated with a water-insoluble organic surface modifier can be prepared by:

collision of the accelerated mixture or collision of the accelerated mixture against a wall of the conduit, thereby obtaining an aqueous dispersion in which the surface modifier is homogeneously dispersed in water;

(a) preparing a mixture of water and a substantially water-insoluble organic surface modifier;

(c) mixing the aqueous dispersion with a pigment, thereby providing a pigment coated with the surface modifier; and

(b) introducing the mixture, under pressure, into a conduit having a diameter-decreased portion and a turning portion wherein the diameter-decreased and turning portions provide accelerated flow through the diameter-decreased portion and mutual

(d) isolating the coated pigment.

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## EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)		
A	EP-A-0 150 776 (MILLIPORE CORP) 7 August 1985 * claims 1,3 *---	1	C09B67/08 C09C3/00 B01F5/06 C09D7/12		
D,A	EP-A-0 544 441 (CIBA GEIGY AG) 2 June 1993 * claim 1 *---	1	//C09D11/02		
A	DATABASE WPI Section Ch, Week 9521 Derwent Publications Ltd., London, GB; Class A25, AN 95-157647 XP002021050 & JP-A-06 279 561 (DAINIPPON INK & CHEM INC), 4 October 1994 * abstract *-----	1			
TECHNICAL FIELDS SEARCHED (Int.Cl.)					
C09B C09C C09D B01F					
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
THE HAGUE	12 December 1996	Niaounakis, M			
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